Effect of Solvent Flow on a Polymer Brush: A Neutron Reflectivity Study of the Brush Height and Chain Density Profile

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We present here the results of neutron and X-ray reflectivity studies on the effects of solvent flow on the height and density profile of polymer chains chemically end-tethered to a surface. Our system consists of perdeuterated polystyrene chains, molar mass 80 000, that were chemically tethered to a silicon oxide surface via trichlorosilane ($SiCl_3$) terminal groups. The brush was exposed to a range of flow rates in both toluene and cyclohexane to a maximum shear rate of 130 000 s^{-1}. We observe that both the polymer brush profile and height remain unchanged even at the highest flow rates and that no loss of polymer occurred. These results are discussed in the context of the various theoretical, simulation, and experimental results presented in the literature.

Introduction

The presence of polymer chains grafted or adsorbed onto a surface can dramatically alter the forces that affect interactions between surfaces. The equilibrium properties of such polymer brush systems have been studied for the past two decades, yielding a generally accepted understanding of the underlying physics.[15,17,19,31,42] Conversely, the nonequilibrium properties of polymer brushes are still the subject of intense theoretical and experimental investigation. Of particular interest is the response of a brush to the frictional forces imposed by macroscopic flow of solvent. The behavior of polymer brushes subjected to flow has important technological implications for the rheology of colloidal dispersions stabilized by polymer layers,[32,40] for the lubrication properties of polymercoated

interfaces,[24] for biocompatibility of medical implant devices, and for permeation flow through polymer-containing porous media.[19,20]

Polymer chains tethered to a two-dimensional surface offer a unique system to study the physics of polymer molecules. The conformation of a polymer chain in a brush exposed to solvent, like that of a free chain in solution, is governed by a competition between two opposing tendencies. One is the elastic contraction as the chains attempt to maximize their entropy by adopting random walk configurations. Competing with contraction are the binary monomer–monomer interactions such as polymer–polymer repulsions and polymer–solvent wetting that tend to stretch the chains.[20,42] Although the forces that determine the properties of tethered chains are the same

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as those for free chains in solution, the scaling properties of tethered polymer chains generally differ from those of free chains.

A free polymer in semidilute solution with N monomers and persistence length b will adopt a conformation that yields a radius of gyration, R_g, that scales as $N^{3/5}b$ in good solvent and $N^{1/2}b$ in a Θ solvent. The density of chains grafted to the surface determines the height, h, of a polymer brush, which is a measure of the linear extension of the chains. In the limit of low surface coverage, measured as the number of chains per unit area or α, the distance between graft sites is greater than the R_g of a free chain in solution. When exposed to solvent, the tethered chains in this so-called *mushroom* regime exhibit swelling similar to that of free chains since the absence of chain overlap yields conformations constrained only by the wall.[42] When the graft density is increased so that $\alpha^{-1/2} < R_g$, interchain repulsions force the chains to stretch away from the surface to minimize these repulsions and maximize interactions with the solvent molecules. In this *stretched* or *brush* regime, h scales as $h \sim N\alpha^x$, where x is an exponent that depends on the solvent quality.[11,15] For a good solvent, $x = 1/3$, whereas in Θ and poor solvents $x = 1/2$ and 1, respectively. Thus, the brush height scales as N, much larger than the radius of gyration of a free chain. Chain stretching in densely grafted brushes has been studied by many different techniques including surface force apparatus,[18,43] neutron reflectivity,[13,22,23] and small-angle neutron scattering (SANS).[3] In general, there is good agreement with results from experiment, simulations, and analytical calculations.[15,17,19,42]

An equivalent understanding of the effects of macroscopic solvent flow on a densely grafted brush has remained elusive despite considerable effort. Rabin and Alexander were the first to develop a theoretical model to describe the behavior of a brush exposed to flow of a good solvent.[38] This model predicts that the chains will elongate in a direction normal to the flow and tilt in the flow direction but that the layer thickness remains "pinned down at the equilibrium value".[38] The model assumes that the brush profile is a step function, the chain ends are at the outer surface of the brush, and all chains behave alike, i.e., the Alexander−de Gennes ansatz. The calculations represent each polymer chain as a string of excluded-volume blobs with a free energy per chain written as a sum of an elastic term involving the conformation of a deformed Gaussian string of blobs and an osmotic term determined by the stretching force.[38] They note that a grafted polymer chain in equilibrium is fully stretched with a blob size controlled by the stretching and not by the interaction with blobs from neighboring chains. This is in contrast to a polymer in semidilute solution that can be represented as a free Gaussian random walk with a step size equal to the blob size and for which the osmotic pressure is concentration-dependent.[28,38]

Using a surface force apparatus, Klein et al.[25,26] measured the normal force between two mica surfaces bearing polymer brushes as they slide past each other. The brush bearing surfaces were separated by a gap containing good solvent. They observed an abrupt increase in the normal force when the relative velocity of the surfaces increased above a critical value, which was

interpreted as a closing of the gap due to brush swelling. Responding to this experimental result, Barrat[7] revisited the Rabin and Alexander model to show that one could in fact predict brush swelling from the earlier model. Indeed, he calculates that under shear the brush would swell to a maximum height 25% greater than the equilibrium height. Barrat approximated the shear flow with a constant force acting at the surface of the brush and argues that this force reduces the osmotic compressibility of the brush, causing it to swell. His approach is essentially similar to that used by Rabin and Alexander but differs in the way the osmotic pressure is calculated. Barrat also predicts that chain extension in the direction of flow is large compared to the increase in brush thickness. For instance, a 150 Å increase in h requires that the chains stretch 2400 Å in the flow direction.[27]

Using the same model, Kumaran predicted a maximum 33% increase in h with high shear.[27] Brush expansion is calculated in two steps using a perturbation analysis. In the first step, the change in the polymer conformations due to the shear flow is calculated following Rabin and Alexander, with the same result. The change in chain conformation from this first step is then substituted into the equations used to calculate the hydrodynamic interactions to calculate δh. The response of the brush to flow is divided into three regimes. For small values of fluid velocity and δh, the brush height is proportional to the square of the fluid velocity at the surface. For intermediate values, brush swelling is a linear function of the fluid velocity, and in the limit of large velocities, brush expansion increases to a maximum of 33% greater than the equilibrium value.[27]

The studies described above model the solvent−brush frictional forces with a shear force applied to the free surface of a brush but essentially ignore the details of solvent flow inside the brush. A quantitative comparison with experiment is not possible because (1) numerical prefactors in the resulting expressions are never explicitly calculated and (2) the effective boundary shear force is experimentally unknown since the relevant experimental control parameter is the shear rate, $\dot{\gamma}$.[20] In a more recent work, Harden and Cates[20,21] attempt to determine in a mutually consistent manner as a function of $\dot{\gamma}$ both the internal structure of a brush and the velocity profile of solvent penetration into a brush in the strong deformation regime. To do this, they also begin with the Alexander−de Gennes model but unlike previous attempts do *not* assume a uniform stretching of the chains. Their approach is restricted to high grafting densities $D \ll R_g \cong N^{3/5}b$, where D ($=\alpha^{-1/2}$) is the mean distance between grafting points, roughly equivalent to the hydrodynamic blob size, ξ_0. They find that the onset of significant brush swelling occurs at $\dot{\gamma}\tau \cong 1$, where $\tau \approx (\eta\xi_0^3)/k_B T$ is the characteristic chain relaxation time for a Gaussian chain in a solvent with viscosity η. Maximum swelling of about 20% occurs for very large values of $\dot{\gamma}\tau \cong 4-5$. Harden and Cates compare their predictions with the experimental results obtained by Klein et al. and state that the experimental parameters reported by Klein, $\tau \cong \eta\xi_0^3/k_B T \cong 2.5 \times 10^{-6}$ s and $\dot{\gamma}\tau = 3/8$, are "roughly a factor of 10 smaller than that required to produce the experimentally reported brush swelling of ~20%."[21] They remark that this discrepancy is not surprising due to the experimental uncertainties in the knowledge of effective viscosity and in the various unknown prefactors and approximations in their model.[20] In a later work, Aubouy, Harden, and Cates[2] relax the Alexander−de Gennes ansatz, allowing for the nonuniformity of chain conformations at equilibrium. Remarkably, they report a greater degree of swelling in the brush

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under shear and a greater degree of susceptibility to solvent flow.

To treat realistically the effects of solvent flow on a brush, a model must describe both the frictional forces exerted on the chains by the moving solvent molecules and how the brush response in turn modifies the solvent flow field inside the layer. The problem essentially becomes a question of hydrodynamic penetration, which depends on the model chosen to describe the brush density profile. The models described above use a step function to model the brush density, rather than the parabolic profile predicted successfully for static brushes by self-consistent-field (SCF) calculations.[15] The first to study hydrodynamic penetration of solvent in a brush with a parabolic profile was Milner.[31] He showed that the hydrodynamic penetration depth, l_p, is much larger for a parabolic density profile than for a step profile. If swelling effects are ignored, Milner found the penetration depth is proportional to the geometric mean of the brush height and the smallest mesh size ξ_0, i.e., $l_p = 1.04(h\xi_0)^{1/2}$. Conversely, if swelling effects are included, the penetration depth becomes $l_p \sim h^{2/5}\xi_0^{3/5}$. For a step function, the hydrodynamic penetration depth is dependent on the mesh size of a semidilute solution or the graft distance, i.e., $l_p \sim \xi_0$.[15] Thus, the penetration depth for a parabolic brush is much greater than for a brush with a step function profile.

Using molecular dynamics (MD) simulations, Grest[14,15] and Peters and Tildesley[36,37] have attempted to model the effects of solvent flow on a brush by including solvent molecules and their interactions. In particular, Grest performed MD calculations on brushes with long chains, $N = 100$. These simulations show no detectable change in either the brush profile or the end-to-end chain distance at low and moderate shear.[15] The simulations show that a small fraction of the chains become strongly stretched along the direction of flow, and there is a slight decrease in h at high flow velocities. However, a large fraction of the chain ends remain buried deep inside the brush and do not feel the effect of shear even at high flow velocities.[15]

In other numerical calculations, the solvent flow field is approximated by hydrodynamic equations for fluid flow in a porous medium. Although the solvent is not included explicitly, its effect is modeled with the Brinkman equation, yielding results that are consistent with the MD simulations described above.[10] Using a bond-fluctuation lattice model in Monte Carlo calculations, Lai and Binder[28] studied the properties of a dense polymer brush in a flow field by modifying the standard Metropolis transition probability to take into account the effective force acting upon the chains by the moving solvent. The brush is assumed to have a parabolic density profile, and the height is calculated in a self-consistent manner. The MC results indicate that in very high flow fields the chains will stretch and tilt in the direction of the flow field causing only a slight decrease in h.[28]

Using an off-lattice MC algorithm, Miao et al.[30] determine self-consistently both brush height and brush density profile in a brush exposed to macroscopic solvent flow. By not assuming a density profile, they avoid one approximation that has plagued previous attempts. However, out of necessity, they also exclude a microscopic representation of the solvent and neglect hydrodynamic interactions between monomers. As in previous studies, they model the solvent as a flow field using the Brinkman equation and assume the brush region behaves as a porous medium with a pore size that is both a local quantity and depends on the time-averaged local monomer density.[30] They state that hydrodynamic penetration is indeed significant and causes the local coils in the blobs to unwind

and aligns the chains as much as possible in the direction of the solvent flow. Thus, the chains are significantly stretched perpendicular to the surface and simultaneously tilted toward the direction of flow such that the overall conformational properties such as average local monomer density and brush height remain unaffected.

While consistent with the MD simulations and the Rabin–Alexander model, these MC results contradict other models and the observations made by Klein. Considerable discussion has been devoted to this discrepancy, which has motivated continuous reanalysis of theory. Doyle et al. point out that the work described by Klein was designed to measure the response of brushes exposed to *oscillatory* shear, whereas the models described above were designed for *steady* shear.[12] In a recent series of Brownian dynamics simulations, Doyle et al. calculate the nonequilibrium brush dynamics in a self-consistent manner under both steady and oscillatory shear of a brush between two walls. They report that under steady shear the brush experiences significant collapse but obtain results consistent with experimental results obtained by Klein et al. for a brush exposed to oscillatory shear. The results obtained by Doyle et al. emphasize the differences between the effects of oscillatory and steady shear on brushes and suggest a possible explanation for the discrepancy between the experimental evidence reported by Klein and the Rabin–Alexander model. Although their prediction of chain collapse under steady shear does not agree with MC and MD calculations, the results obtained by Doyle are consistent with other Brownian dynamics simulations reported by Saphiannikova et al.[41]

Much of the work discussed above has focused on brushes in good solvent conditions, with relatively little attention given to brushes in other solvents. For a brush in Θ solvent, both Barrat and Kumaran predict that the brush height is unaffected by fluid flow since hydrodynamic interactions are screened over a very short distance.[7,27] Using the same Rabin–Alexander model, Williams[45] predicts that a brush at low grafting density will undergo compression with flow in a poor solvent, i.e., Θ solvent below the Θ temperature. Parnas and Cohen also employed Brownian dynamics simulations to calculate both the segment density and fluid velocity profiles self-consistently of a single tethered chain in Θ solvent.[34,35] They find that the thickness of a model polymer layer is a strong function of the shear rate and chain length. For the longest chains studied, i.e., equivalent to $M_w = 4 \times 10^4\,\text{g mol}^{-1}$, the thickness of the model polymer increased up to a shear of about $1000\ \text{s}^{-1}$ and then decreased at higher shear values. In addition, the segment density distribution and normal stresses are sensitive to low values of shear.

A review of the theoretical literature shows that a description of the response of polymer brushes to solvent flow has been difficult to obtain. Historically, Rabin and Alexander[38] proposed a simple model of brush response to flow of good solvent, predicting chain stretch and tilting in such a way to produce no observable effect in the brush height and density profile. Following the measurements of Klein et al.,[24-26] others have modified the original Rabin–Alexander treatment in an attempt to model swelling behavior interpreted from the experimental findings. These efforts predict varying degrees of brush swelling. Indeed, some predict a maximum increase of 33% at the highest shear values, with observable swelling

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effects at low and moderate shear.[27] Interestingly, there has been no theoretical prediction for the properties of a brush under shear using the self-consistent-field approach that has correctly predicted the static properties of a brush.[15] The picture emerging from MD and MC simulations appears to be more consistent with the Rabin– Alexander predictions.[14–17,28,30] However, Brownian dynamics simulations of brushes exposed to good solvent predict significant brush compression in response to flow.[12] The literature contains relatively little information describing the effects of the flow of Θ solvent, with contradictory predictions for the attempts that have been made.

Clearly, the literature contains a confusing picture of the nonequilibrium behavior of tethered polymer chains, and we require reliable *direct* experimental results that unambiguously demonstrate brush response to high shear fields. Experimentally, the only direct measurements of the density profile and brush height in a steady shear flow are the neutron reflectivity measurements by Nguyen et al.[33] and Baker et al.[4,5] In the former, a polymer brush was exposed to a maximum shear rate of 7500 s^{-1} by a flowing solvent. They find that the brush height remained independent of shear, but the maximum shear rate achieved in this study does not access a regime of consequence.[15] Baker et al. achieved a shear rate of 10^4 s^{-1} with adsorbed polystyrene–poly(ethylene oxide) (PS– PEO) block copolymer brushes on a silica surface in toluene and also report little or no effect of shear on the brush height. They also report achieving a shear rate of 2×10^4 s^{-1}, but this was accompanied by significant desorption of the brush. Since the binding energy is of order 10 $k_B T$, the adsorbed PS–PEO block copolymer brushes have a tendency to come off the surface at some "critical" shear rate roughly estimated between 1.5×10^4 and 2×10^4 s^{-1}.[5] They further state that their results lend support to the modified model developed by Aubouy, Harden, and Cates wherein the Alexander–de Gennes ansatz was partially relaxed to calculate the effects of shear on end-adsorbed block copolymer brushes.[2,5] The model predicts a strong increase in desorption at the swelling transition, leading to a catastrophic removal of chains from the interface.[5,2] Ellipsometric measurements of polystyrene (molar mass = 20×10^6) in a Θ solvent showed that the root-mean-square (rms) thickness decreased by about 15% as the shear was increased to 8000 s^{-1}, but polystyrene with molar mass $\leq 8.6 \times 10^6$ revealed no change in rms thickness in this shear regime.[29] Other experiments utilizing indirect measurements of the brush height suggest that h is independent of shear rate[44] or that brush thickening occurs.[24]

We have measured directly the effects of solvent flow at shear values 1 order of magnitude higher than previously reported. To distinguish among the various theoretical, simulations, and experimental results, we use neutron reflectivity to measure the profile of a dense chemically grafted polystyrene brush exposed to flow of both good solvent (toluene) and Θ solvent (cyclohexane) in a range of shear values up to 130 000 s^{-1}. We observe no loss of polymer from the surface, nor do we observe any change in the brush profile or height with shear.

Experiment

Our neutron reflectivity experiments measure the segment density profile of polymer brushes under shear in an experimental cell similar to that used by Baker et al.[6] The cell is designed to have plane Poiseuille flow with both walls stationary and the fluid pumped between them. We describe briefly the cell since it includes modifications we have made for this work. The cell consists of a polished single crystal silicon block with a 3 cm thickness and tethering surface approximately 8 × 14 cm. The other wall consists of a stainless steel block with similar dimensions and fluid reservoir, holes, and groove machined after Baker et al.[6] The gap between the two walls is variable and determined by the thickness of a gasket cut from poly(tetrafluoroethylene) (PTFE) film. The two halves and gasket are held together by a clamp made of nylon. Each half of the clamp contains a fluid reservoir for circulating coolant across both the silicon crystal and steel block in order to regulate the experimental temperature. For this study, the gap was set to either 0.25 or 0.05 mm ± 10%, measured after assembly. We estimate the shear at the brush surface using flow velocity data measured with the assembled cell for each gasket and by using standard expressions for laminar flow of Newtonian fluids that describe fluid flow with a parabolic profile in the gap between the walls.[8] The maximum measured flow rate accessible with the 0.25 mm gasket is 24.0 cm^3 s^{-1}, yielding an estimated shear of 30 000 s^{-1}. For the 0.05 mm gasket, the maximum measured flow rate is 3.94 cm^3 s^{-1}, which gives an estimated shear at the surface of 130 000 s^{-1}. We measured the reflectivity of the brush using several flow rates from 0 s^{-1} to the maximum value for each cell configuration.

Our polymer brush consisted of deuterated polystyrene (d-PS) with a trichlorosilane (SiCl$_3$) end group to bind chemically the chains onto the single-crystal Si surface. The Si crystal was cleaned in a heated bath of 70% H$_2$SO$_4$/30% H$_2$O$_2$ prior to brush adsorption.[22] The molar mass of the deuterated polystyrene used in our experiment is 83 000. The SiCl$_3$ end group offers a high binding energy ($\cong 10^2 kT$) and allows us to control the grafting density by varying the reaction time and solution conditions.[22] To prepare the brush, we expose the clean silicon crystal surface to a solution containing ~200 mg of polymer in ~100 mL of cyclohexane for 12–72 h at 4 °C. Excess unbound polymer was removed by washing repeatedly with toluene and dichloromethane, followed by an extended wash (~8 days) with toluene. All measurements were taken at ambient temperature (~22 °C), except one series taken with cyclohexane at 130 000 s^{-1} with the temperature controlled at 30 ± 0.2 °C, the Θ temperature for d-PS in hydrogenous cyclohexane.[9]

The neutron reflectivity (NR) measurements were performed at the NG7 horizontal reflectometer located at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). Measurements were performed with the incident neutron beam entering through one edge of the silicon crystal and reflecting from the silicon–polymer–solvent interface. The reflected beam traversed back through the crystal to the detector. We obtained specular neutron reflectivity from the brush as a function of wave-vector transfer $Q = 4\pi(\sin\theta)/\lambda$, where θ is the angle of incidence and reflection of the neutron beam and a fixed neutron wavelength $\lambda = 4.76$ Å and $\delta Q/Q = 0.04$. Details of the NR technique and instrumentation are described elsewhere.[1,39]

Results and Discussion

The dry brush height was measured by X-ray reflectometry both before and after neutron reflectometry (NR) measurements. No appreciable differences were observed in the reflectivity profiles after shear, indicating no loss of polymer. The thickness of the dry layer was determined by X-ray reflectometry to be 175 Å. This gives a coverage, $\Gamma \sim 18$ mg/m^2, or in terms of a dimensionless grafting density, $\sigma = (b/D)^2 = 0.057$, where $b = 6.7$ Å is the statistical segment size and $D = 28$ Å is the average distance between grafting sites.[22] After Kent et al.,[23] we can calculate a reduced surface density, $\Sigma = D^{-2}\pi R_g^2 \cong 25$, where R_g ($\cong 80$ Å) is the radius of gyration of a free Gaussian random walk in dilute solution. In other words, the surface density of chains in our system is 25 times greater than what is necessary to cause chain overlap in a solution of Gaussian free chains.

In general, oscillations in X-ray and neutron reflectivity profiles yield a characteristic thickness of the brush. From reflectivity theory, the brush thickness can be directly obtained from the position of two successive minima using
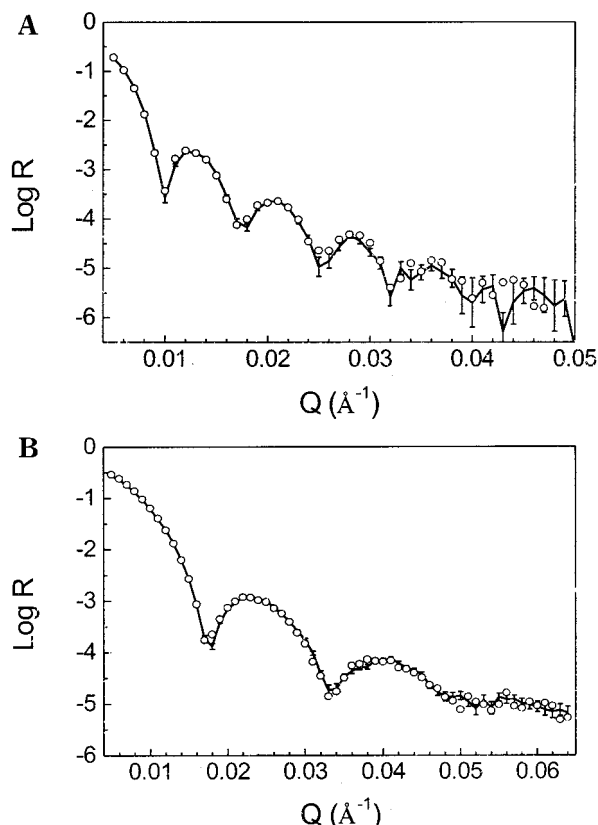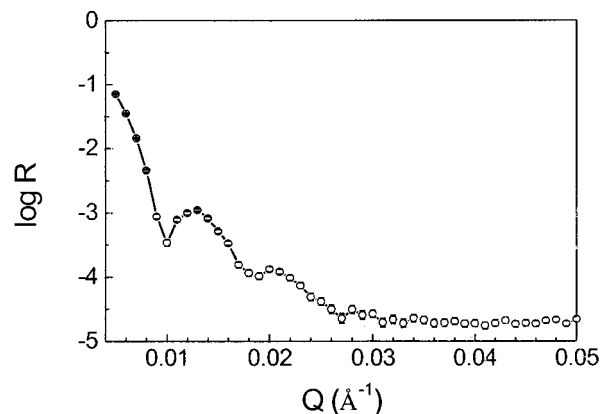
Figure 1. (A) NR data for d-PS brush in toluene at 0 s^{-1} shear (solid line) and 30 000 s^{-1} (open circles) with a 0.25 mm gap. Position and spacing of Keissig fringes give a 750 Å layer. (B) NR data for shear in cyclohexane. Symbols have the same meaning as (A). Height of brush layer is 310 Å.

Figure 2. NR data for d-PS brush in toluene at 0 s^{-1} (solid line) and 1.3×10^5 s^{-1} (open circles).

the relation $d = 2\pi/Q_{1,2}$ where Q_x denotes the position of the x minimum. Thus, both the position and separation of minima represent a sensitive measure of the brush height, h, while the overall reflectivity profile is a measure of the segment density distribution throughout the layer. Figure 1 compares the reflectivity of the brush layer exposed to a moderate shear, 3×10^4 s^{-1}, with the equilibrium value, i.e., no shear, in both toluene (Figure 1A) and cyclohexane (Figure 1B). Although measurements were taken at a range of shear values, we display only data obtained at the highest shear for each cell configuration since all our measurements show no change when compared with data obtained at equilibrium. From the data, we estimate that the equilibrium brush height in both cyclohexane and toluene is 310 and 750 Å, respectively. These values of height are significantly greater than in air and suggest we are well into the "brush regime". However, the data also show no change with shear for either toluene or cyclohexane, a clear indication that neither the brush height nor segment density profile changes with moderate shear.

Figure 2 compares the neutron reflectivity of our d-PS brush in toluene at equilibrium and exposed to a shear of 130 000 s^{-1}. Again, only the highest shear value is compared against the equilibrium result. We interpret these results to mean that, to within experimental uncertainties and instrument resolution ($\sim$2−3%), both the brush profile and height remain unchanged. We also emphasize that these results clearly show no loss of polymer even when the brush is exposed to the highest solvent flows.

A comparison of Figures 1A and 2 reveals significant differences in the reflectivity profiles obtained from the brush using the 0.25 and 0.05 mm gap configurations. These differences are due to increased neutron scattering from the steel surface. Since toluene possesses a neutron $1/e$ transmission of 0.272 cm, a sufficient number of neutrons penetrate far enough into the solvent to scatter from the steel surface and back into the detector. This increased "background" reduces our ability to resolve to low reflectivities by significantly reducing the signal-to-noise. In cyclohexane the effect is much less pronounced (cf. Figures 1B and 3) since cyclohexane possesses a $1/e$ neutron transmission of 0.184 cm. Thus, with cyclohexane fewer neutrons penetrate far enough into the solvent to reflect from the steel surface into the detector to noticeably contribute to the background signal already present from incoherent hydrogen scattering coming from the solvent. Notwithstanding the increased background observed with toluene, the reduced signal-to-noise does not sufficiently degrade the data to preclude an unambiguous comparison with and without shear.

In Figure 3A we compare shear results for the brush in cyclohexane taken at equilibrium and the highest shear, 130 000 s^{-1}, using a 0.05 mm gap. The cell temperature was monitored using a standard thermocouple, but we did not control the temperature for this measurement. Contrary to the result with toluene, we see changes that reflect brush thickening in this solvent when the system is exposed to high shear. The spacing and positions of the minima in the reflectivity profiles in Figure 3A indicate a $\delta h = 12$ Å, which represents an increase of 3−4% of the brush height. Thus, with our measurements, we are able to detect subtle changes in the brush height, when they occur. However, our in-situ temperature measurements of the silicon block also show a 3 °C increase above ambient temperature accompanying the highest solvent flow rates as a result of frictional heating. We expect that increasing the temperature of a Θ solvent−polymer system will induce swelling as a direct result of improved solvent− polymer interactions. Indeed, the degree of brush swelling we observe in cyclohexane is quantitatively consistent with results reported by Karim et al.[22] for polystyrene in a Θ solvent at elevated temperatures. Figure 3B shows the results of another series of similar measurements in which the cell temperature was maintained and monitored at 30 °C, the Θ temperature for deuterated polystyrene in hydrogenous cyclohexane.[9] We note that the reflectivity profile of the brush exposed to high shear is identical with the equilibrium profile. From these results, we conclude that the swelling we observe in cyclohexane at high shear is due to heating and does not represent a direct effect of shear. These results emphasize the importance of temperature stability, especially for polymers in thermal
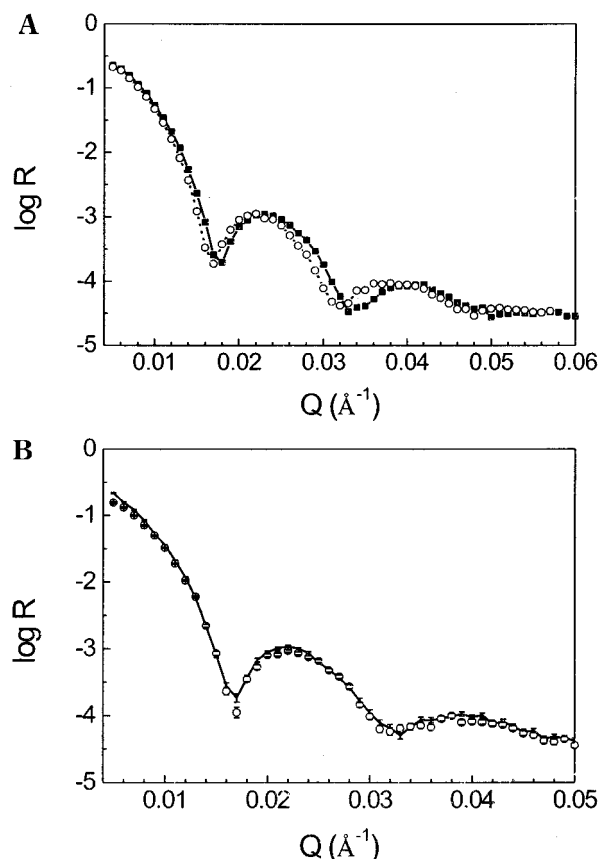
Figure 3. (A) NR data for d-PS brush in cyclohexane at 0 (filled squares) and 1.3×10^5 s^{-1} (open circles). Lines are drawn as a guide to the eye. Data taken with no temperature control. (B) NR data taken with cell temperature regulated at 30 °C; solid line represents data taken for cyclohexane at 0 s^{-1}, and open circles are 1.3×10^5 s^{-1}.

solvents. A similar result is not expected with toluene since temperatures in the range 20−30 °C are well into the good solvent regime for this polymer−solvent pair.

The results presented in this work clearly demonstrate that the thickness and density profile of a chemically tethered polymer brush remain unaffected by solvent flow, even to high shear rates. A direct comparison of these results with previous work is possible only with other similar experiments, namely those obtained by Baker et al.[4,5] Although they used a similar sample apparatus, their use of physically adsorbed, or grafted, polymer chains prevented access to shear rates higher than 2×10^4 s^{-1}, at which point loss of polymer was observed. Although they failed to see any swelling in good solvent, they suggest that their results are consistent with a model proposed by Aubuoy, Harden, and Cates[2] that predicts a discontinuous swelling transition at a certain critical shear rate for *grafted* chains, which occurs just prior to chain desorption. The brush system presented in our work consists of *chemically* end-tethered chains and shows no evidence of any brush swelling, compression, or polymer loss at shear rates approaching 130 000 s^{-1}.

Comparison with many theories presented in the literature is difficult since the descriptions rarely include parameters experimentally accessible. Nevertheless, we note that Barrat[7] predicts a brush will swell to a maximum height 25% greater than the equilibrium value under high shear, and Kumaran[27] calculates an increase in the brush height for a wide range of shear rates. As described in the Introduction, Kumaran finds the brush height is a function of the fluid velocity at the surface, with h increasing in

proportion to the square of fluid velocity for low values and expanding to a maximum of 33% greater than the equilibrium value at high flow. In the range of 0−130 000 s^{-1}, we observe no change in the brush height. While we are not able to determine the fluid velocity at the surface, it is reasonable to conclude that we have accessed at least one of the regimes Kumaran describes and even some portion of the swelling regime described by Barrat. Since we can clearly resolve a 3−4% change in the brush height, we conclude that our measurements do not support the predictions of these two models.

To compare our results with other theoretical and simulation predictions, e.g., Harden and Cates, etc., we require the Weissenberg number, W_i, a product of the shear rate, $\dot{\gamma}$, and the characteristic relaxation time, τ, of a tethered chain. Typically one expects to observe shear effects occur when $W_i \geq 1$.[15,21] While we can calculate the shear rate using our measured flow rate data and standard hydrodynamic relations, a determination of the characteristic relaxation time is considerably more problematic. The point of departure in discussions of the characteristic relaxation time for tethered chains is the description of an isolated Gaussian chain in semidilute solution, $\tau \approx (\eta \xi_0^3)/k_B T$. Here η is the solvent viscosity, and ξ_0 is the hydrodynamic blob size, which is assumed to be roughly equivalent to the mean distance between grafting points for tethered chains. Use of this free-chain expression to describe the relaxation time of densely tethered chains requires appropriate prefactors, which Harden and Cates[20,21] leave undetermined, but others such as Grest[15] and Doyle et al.[12] report $4\pi^3$ and $3\pi(5.7)$, respectively. Assuming $\xi_0 = D = 28$ Å and using our experimental parameters, we obtain $\tau = 4\pi^3 \eta \xi_0^3/k_B T = 3.9 \times 10^{-5}$ s for the former. This gives $W_i \approx 5$, well within the range predicted by Harden and Cates and others to produce a pronounced effect on tethered chains. Indeed, Harden and Cates predict a 20% increase in brush height for this range of Weissenberg number.

Alternatively, if we use the value employed by Doyle et al., we obtain $\tau = 3\pi(5.7)\eta \xi_0^3/k_B T = 1.7 \times 10^{-5}$ s with $W_i \cong 2$ for $\dot{\gamma} = 1.3 \times 10^5$ s^{-1}. For this model, they show that the brush remains at its equilibrium thickness until W_i exceeds 0.1, at which point significant brush compression is observed. For example, for $W_i = 0.17$, the brush height is reduced by 15%. By comparison, our measurements access a shear regime ∼12 times greater, well within the range expected to produce observable brush compression.

It is worth noting that $W_i \propto \xi^3$, which is assumed to correspond to the distance between graft sites on the surface. To date, our measurements have focused on maximizing W_i through increased shear, $\dot{\gamma}$, since this allows us to achieve reasonably high values of W_i without sacrificing signal. One can also increase W_i by increasing the characteristic relaxation time by reducing the graft density, say a factor of 2, which would increase the distance between graft sites and therefore W_i by $2^{3/2}$. It is conceivable that such an increase will noticeably perturb the chain profile; however, we believe this is unlikely since the increase is less than an order of magnitude over what we have already achieved. Furthermore, such reductions in the chain density will be accompanied by a significant reduction in the contrast of the system and compromise our ability to measure accurately the chain profile.

As described in the Introduction, not all models presented in the literature predict an observable effect on the macroscopic properties of a brush. Specifically, we return to the model originally presented by Rabin and Alexander. They predict that polymer chains exposed to solvent flow will stretch in a direction normal to the flow

and tilt in the flow direction but that the layer thickness will remain essentially at the equilibrium value. This result has been further supported by the Monte Carlo predictions by Miao et al.[30] The molecular dynamics simulations of Grest[14-17] and Peters and Tildesley[36,37] predict a slight decrease in the layer height at high shear. They also suggest that a few chains will be strongly stretched in a manner consistent with the Rabin–Alexander model and MC results, while the majority of chain ends will remain buried in the layer. Our results conclusively support the prediction that the brush height and density profiles remain unchanged in the presence of solvent flow. However, we cannot yet determine the effects of solvent flow on chain ends or if the chains are stretched in the direction normal to the flow and tilted in the direction of flow. A study designed to answer this question is currently underway.

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